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THE CATALYSIS OF HYDRAZINE

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16. Abstract Hydrazine sulfate in a hot aqueous solution can be catalyzed in the direction of $3 \text{N}_2\text{H}_4 = 4 \text{NH}_3 + \text{N}_2$. Free hydrazine in a hot aqueous solution dissociates in the presence of platinum in the following direction: $2 \text{N}_2\text{H}_4 = 2 \text{NH}_3 + \text{N}_2 + \text{H}_2$. In the presence of sodium hydroxide, the catalytic dissociation of hydrazine takes a third direction: $3 \text{N}_2\text{H}_4 = 2 \text{NH}_3 + 2 \text{N}_3 + 3 \text{H}_2$.			
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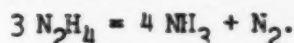
THE CATALYSIS OF HYDRAZINES

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In a previous report [1] I stated that hydrazine sulfate in a hot aqueous solution can be catalyzed by means of platinum in the direction of

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The catalytic dissociation of free hydrazine follows a different course.

A hot solution of hydrazine sulfate can be dissociated by hydrate of barium so that the least possible amount of barium remains in the solution. Following draining and rinsing, I diluted the filtrate up to 250 cm³. This solution was heated in a Wurtz flask set in a water bath. When necessary, I added water so that the solution always reached the neck of the flask. Thereafter 0.2 to 0.3 gram of platinum were added and the gas developing was collected through water into a metering cylinder kept ready. The gas development started at once and was rapid at first but slowed down later on. After 6 to 7 hours it was so slow that hardly even 10 cm³ could be collected over a period of one hour. In order to convert the hydrazine until only traces remain, it was necessary to keep heating for more than 24 hours. I usually interrupted the operation after 7 to 10 hours and examined the dissociation products. The volume of gas collected demonstrated clearly that the dissociation did not follow the same patters as that of the hydrazine salt. While a dissociation in that direction set free 57.4 cm³ of nitrogen from each gram of hydrazine sulfate, 3 g. hydrazine sulfate gave in this case rise to 450 cm³ gas and 5 g. hydrazine sulfate to 750 cm³ gas.

* Numbers in the margin indicate the pagination in the foreign text.

In both cases 0.27 g and 0.35 g, respectively, of hydrazine were still present in the solution.¹ The volumes indicated become evident after the necessary corrections for temperature, barometric pressure and vapor pressure. In addition, 9 cm³ must first be deducted from the gas volume measured, since two blank tests, executed under conditions as far as possible identical while using water only, have shown that according to my experience, 9 cm³ of air are driven out of the flask after the addition of platinum and heating for one hour in the water bath. In part, this air originates from the platinum; in part it is driven out of the flask because of expansion and an increase in the vapor pressure. I performed this experiment in order to find out whether the content of air in the platinum affected the amount of gas collected. The correction as such is not very exact since during the experiment with hydrazine the vapor pressure of ammonia must also be added.

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The gas collected did not contain any nitrous oxide, nor any carbon dioxide or carbon monoxide and it was not absorbed by concentrated sulfuric acid. Hydrobromic acid did not affect it either. When mixed with oxygen, it deflagrated within the absorption tube.

Amount of gas	Amount of gas + O ₂	Amount following deflagration	+ H ₂
33 cm ³	49.5	24	51.51
34	53	27	50.94
30	44	21	51.06
39	59	29.5	54.41
27	41	21	49.60

Several experiments proved that only one third of the reduction in volume following the deflagration depends on the disappearance of the oxygen. I have estimated how much oxygen should be freed, determined eudiometrically the amount of oxygen released and compared the result with my calculation:

¹I.E., when titrated with a potassium permanganate solution, the titer of which was determined by the amount of hydrazine sulfate weighed. Thereby it is of no consequence how the potassium permanganate affects the hydrazine.

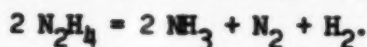
The gas contains 50% hydrogen². The other half of the gas consists of nitrogen. However, it was not excluded that it could be a mixture of equal volumes of free nitrogen and free hydrogen rather than a gaseous NH compound, since during the combustion of such a compound the volumetric relationship would not be different. However, the reaction behavior of the gas together with the reagents mentioned seems to contradict the hypothesis of a nitrogen - hydrogen bond. Therefore I tried to accomplish a separation of the gas mixture into its components. For this purpose I utilized the different capacities of these gases for diffusion. I constructed the small device illustrated below, forced out the air from the outer as well as the inner cylinders by means of carbon dioxide and allowed thereafter a slow flow of carbon dioxide to pass through the inner cylinder, while the outer one was filling up with test gas. The gas in the inner cylinder was collected in a gasometer, freed from carbon dioxide and analyzed:

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Amount of gas	Amount of gas + air	Amount following deflagration	% H ₂
14 cm ³	45	30	71.42
31	89	54	75.22

I obtained 450 cm³ of gas containing 50% hydrogen, subject to diffusion, and 90 cm³ gas with a content of 71.5 up to 75% hydrogen.

Thus, free hydrazine in a hot aqueous solution dissociates in the presence of platinum in the following direction:



² It is well known that when hydrogen is consumed, the admixture of nitrogen is at least in part oxidized by the excess of oxygen. Therefore the amount of hydrogen in the gas will be larger, the more oxygen is used up.

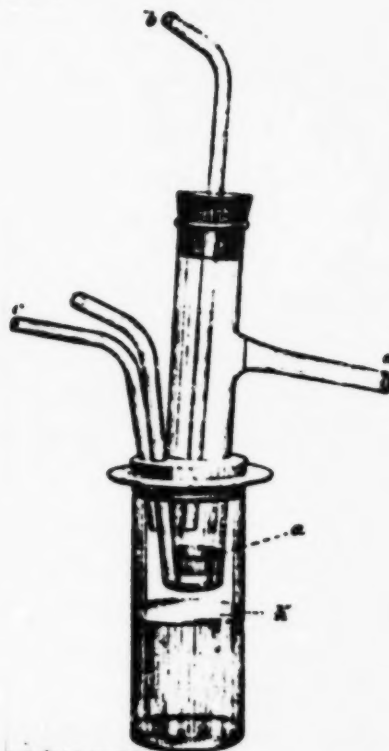


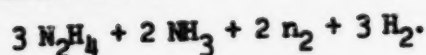
Fig. 1. a) glass stopper; b) CO₂ inlet; c) gas mixture intake; d) outlet to the gasometer; K) cylinder of mercury.

The volume of gas developed, beside the apparent appearance of ammonia as a break-down product, is in favor of the equation described.

It could also be that a small amount of hydrazine could be dissociated in an acid solution in the same direction, but in that case I was unable to confirm the appearance of hydrogen. In the device described above, I subjected the gas, developed during the catalysis, to diffusion, whereby, following double diffusion, 30 cm³ of diffused gas were obtained from 350 cm³. However, this fraction did not react with oxygen in the absorption tube. Consequently, the nitrogen appearing due to this kind of catalysis cannot contain more than 1% of hydrogen.

In the presence of sodium hydroxide the catalytic dissociation of the hydrazine takes a third direction:

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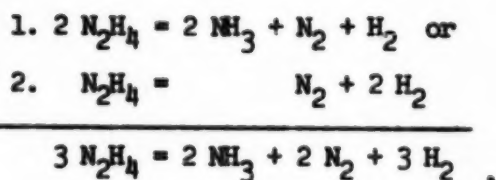
To an aqueous solution of free hydrazine, prepared from 3 g hydrazine sulfate, 7 to 9 g of solid sodium hydroxide were added and catalyzed as usually. The gas volume collected was much larger than during the catalysis without sodium hydroxide, i.e., between 775 and 820 cm³ depending on the duration of the operation since, also in this case, the dissociation proceeds very slowly and I did not let it come to completion. When analyzed, the gas collected was as follows:

Amount of gas	Amount of gas + O ₂	Amount following deflagration	% H ₂
35 cm ³	55.5	24.2	59.60
35	59	27	60.91
30	47	20	60.0
28.5	47.5	21.5	60.77

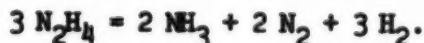
I also fractionated the gas while collecting it and discovered that it was uniformly composed throughout the dissociation. The excess hydrogen could in this case possibly originate from the ammonia, which could be catalyzed by the platinum in the presence of sodium hydroxide. However, the experiment

revealed that the ammonia did not dissociate under these conditions. In order to make the conditions as comparable as possible, I used ammonium sulfate (5 g), added sodium hydroxide in excess and tried to catalyze this with platinum. During three hours I did not collect more gas than during the blank tests of this kind. The gas did not contain any hydrogen.

That possibility had also to be tested, i.e., whether hydrazine in a strongly alkaline solution would not dissociate just into its components, $N_2 + H_2$. This could result in a gas with about 66% hydrogen. However, since at the concentration of alkali indicated, the reaction can take two directions at the same speed:



this dissociation cannot be distinguished from that in the direction:



However, continued experiments with the catalysis of hydrazine in variously strong alkaline solutions demonstrated that the prevalence of a dissociation in the direction $N_2H_4 = N_2 + H_2$ was in no case noticeable, since the content of hydrogen in the gas, developed due to dissociation, never exceeded 60%. This shows that hydrazine does not dissociate in the direction suggested. These tests displayed, however, some additional peculiarities.

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Five grams of hydrazine sulfate were catalyzed in the usual manner after adding 4.5 g of solid sodium hydroxide. Since the amount of sodium hydroxide was adequate for completely dissociating the salt and to release the hydrazine I expected that the dissociation should follow the same course as that of free hydrazine. However, already a small amount of the gas collected revealed the opposite. The hydrogen content of this gas did not amount to more than 9.5%. Further experiments with increased quantities of sodium hydroxide demonstrated that the volume as well as the hydrogen content of the gas increased uniformly. When using 5.5 g of sodium hydroxide, the gas held 24%

hydrogen; at 7 g it contained 35%, at 9 g 50% and at 14 g 57% hydrogen. When 15 g sodium hydroxide per 3 g hydrazine sulfate were used, the hydrogen content rose to 60% but further addition of the alkali did not alter the composition of the gas.

15 g NaOH per 3 g $N_2H_4 \cdot H_2SO_4$

Amount of gas	Amount of gas + O_2	Amount following deflagration	% H_2
36.5 cm ³	58	24.5	61
47	67.5	25	60.4
35	53	22	59.03

25 g NaOH per 3 g $N_2H_4 \cdot H_2SO_4$

30 cm ³	62	35	60
27	40	15.5	60.5
35	54	22.5	60

This behavior can be understood if it is assumed that a large excess of alkali is necessary in order to completely release the bases from the hydrazine; at equivalent amounts of hydrazine and alkali there is a division of the acid on both parties so that the catalysis will concern mainly the bonded hydrazine. At an increasing content of alkali, the amount of free hydrazine in the solution increases and the direction of the dissociation approaches, in addition, that of free hydrazine. Since the different speeds of the dissociation in the different directions and, thus, also the different speeds of the changes in concentration of the components in solution are added, the conditions become very complex and no simple correlation between the alkalinity of the solution and the composition of the gas can be expected.

Finally, I have to mention that still another problem has occupied me. The appearance of more hydrogen than required for the dissociation in the direction of $2 N_2H_4 = 2 NH_3 + N_2 + H_2$ could also depend on the condition that, beside ammonia, an oxygen compound, poor in hydrogen, could develop. I assumed it could be a nitrogen compound, N_4H_2 , analogous to solid phosphoric hydrogen. However, there are no guiding principles for justifying

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such a hypothesis. What remains in the solution after the interruption of the dissociation has proven to consist of unaltered hydrazine, independent of whether the dissociation is interrupted sooner or later. In order to distinguish hydrazine from a N_4H_2 compound, possible existing, I used potassium permanganate for the oxidation and applied the correlation between the volume of nitrogen developed and the volume of potassium permanganate used as criterium.

Odessa, Russia, the Chemical Laboratory
of the Neorussian University, April
5th - 18th, 1902.

Bibliography

1. Tanatar, S., Z. phys. Chem. 40, 475 (1902)

ADDENDUM

In the preceding report I stated that cases where the direction of the reaction was apparently altered by the catalysts had not been tested. It has to be mentioned that Ipatieff in the course of his investigation of pyrogenic contact reactions of alcohols observed that such reactions proceeded in different directions in the presence of different bodies.

It must also be emphasized that I overlooked that Prof. Ostwald himself has taken the case of selective catalysis into consideration. See: Ostwald: "On Catalysis", Verhandl. d. Gesellsch. Deutscher Naturforscher und Aerzte, a review of the book by Lassar-Cohn: Arbeitsmethode fuer organisch-chemische Laboratorien [Manual for organic-chemistry laboratories], Z. phys. Chem. 40, 120 (1902).